Chemical Mapping of the Marine Microlayer: A System for Measurement of Spatial and Temporal Variations in Composition

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LONG-TERM GOALS

The viscoelastic behavior of the air-sea interface, a key parameter affecting air-sea exchange of mass, momentum and heat, is strongly dependent on naturally-occurring adsorbed surfactant materials (Frew, 1997; Frew *et al.*, 2001). My long-term goals are to understand the relationship between the composition of surface-active organic matter in the marine microlayer and the viscoelasticity of the sea surface and to delineate the role of microlayer films in modulating roughness and near-surface turbulence.

OBJECTIVES

The occurrence, spatial distribution, concentration and composition of sea surface films are not well known. In order to understand and model the impact of the surface microlayer on air-sea exchange processes, it is useful to have detailed information about the following:

- film formation rates and persistence as a function of wind stress;
- patchiness of film distributions over a range of spatial scales (10m – 1 km);
- surface tension and elasticity variations on these spatial scales;
- film composition as a function of film pressure, wind stress, and seasonal factors.

In order to develop such information, this project focuses on designing and deploying systems to detect and measure organic analytes in the marine microlayer in near-real time. Responding to a broad range of organic compounds, such systems can provide specific information on the composition and structure of surface-active materials and estimates of surface enrichments of specific surfactants that control the viscoelasticity of the sea surface.

APPROACH

A new survey tool, SCIMS (Slick Chemical Identification and Measurement System), which detects the presence of surface microlayer films and allows mapping their spatial and temporal distributions, is being deployed for seasonally-distributed observations at the Marthas Vineyard Coastal Observatory site off Cape Cod (MVCO; http://www.whoi.edu/science/AOPE/airsea/observatory.htm). SCIMS consists of a surface microlayer skimmer that is coupled to a fluorometry package and an automated

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14. ABSTRACT

The viscoelastic behavior of the air-sea interface, a key parameter affecting air-sea exchange of mass, momentum and heat, is strongly dependent on naturally-occurring adsorbed surfactant materials (Frew, 1997; Frew et al., 2001). My long-term goals are to understand the relationship between the composition of surface-active organic matter in the marine microlayer and the viscoelasticity of the sea surface and to delineate the role of microlayer films in modulating roughness and near-surface turbulence.

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extraction interface. It is used in conjunction with innovative ion trap mass spectrometry technology to study microlayer film accumulations and their specific composition. Deployed on a remotely-piloted catamaran, SCIMS processes the skimmer flow stream, carrying out cyclical, microscale solid-phase extraction, concentration, desalting, and elution of microlayer surface-active organics for short-term archiving in an autosampler-compatible vial array. The time-series 'snapshots' of the extracted microlayer are then processed by a shipboard ion trap mass spectrometer (ITMS) to develop the surface compositional profile of the area surveyed by the skimmer, with a temporal resolution of about ten minutes. The mass spectral information can be further used with elasticity data to develop correlative relationships between film composition and elasticity. SCIMS also provides real-time measurements of microlayer and subsurface colored dissolved organic matter (CDOM) fluorescence with 1-second resolution.

WORK COMPLETED

A semi-autonomous vehicle to deploy SCIMS was designed, constructed, and tested extensively. SCIMS and its vehicle were successfully deployed four times in the MVCO study area, twice in June, 2001 from the R/V Oceanus and twice from the R/V Asterias during the July/August, 2001 CBLAST-LOW pilot experiment, the latter coincident with LongEZ overflights. A total of fifty sample extracts and fourteen hours of fluorescence data were collected during these deployments. To date, the fluorescence data from these deployments have been fully processed to provide estimates of microlayer surface excess CDOM and preliminary screening of the SCIMS extracts by electrospray mass spectrometry has been completed .

RESULTS

The remote vehicle is a thirteen-foot catamaran supporting an instrument platform on which the SCIMS package, two GPS units, battery banks, and solid-state chargers are mounted. Twin radio-controlled electric motors and servo-driven rudders provide propulsion and steering. In addition to SCIMS, the vehicle carries a flux measurement system consisting of a 2-D sonic anemometer and relative humidity gauge mounted on a 3-meter mast and a subsurface temperature and conductivity probe. The GPS units are integrated with the data acquisition systems. Communications and real-time control of SCIMS operations are made via wireless components mounted on the catamaran and the support vessel. In deployments, the vehicle proved to be highly maneuverable in winds up to 6 m/s and generally operated as envisioned. Endurance was about 6 hours and limited mainly by the current drain of the propulsion system. Some problems with poor signal range and dropout of the wireless link were experienced, particularly during swell conditions. These were attributed to the relatively planar broadcast/reception characteristics of the antennas used. Tests of an improved omnidirectional antenna that should alleviate this problem are underway.

All four SCIMS deployments took place under low-to-moderate wind and sea state conditions, with winds from 1-5 m/s and 2-3 ft swell. Figure 1 shows the microlayer surface excess CDOM calculated from microlayer-subsurface CDOM fluorescence differences along a 2.5-hour track (inset) surveyed on August 1, 2001 (yearday 213) as part of the CBLAST-LOW pilot experiment. These data were acquired at 1 Hz and were calibrated as parts per billion of quinine sulfate (ppb q.s.), which was used as an external fluorescence standard. Positive surface enrichments were observed along the entire track, ranging from ~ 0.01-0.23 ppb q.s. Surface excess distributions were extremely patchy, with enrichment features from a few tens of meters to several hundred meters in scale. Over larger scales (~ 1-2 km), surface enrichments generally decreased along the southwestward leg (Leg 1) and increased

along the southeastward leg (Leg 2). Based on previously published data, the observed surface excess CDOM variations imply large changes in ripple damping, with expected reductions in degree of saturation, β, of 1-2 orders of magnitude at wavenumber $k = 400$ rad/m (Bock *et al.*, 1999). These reductions in turn imply strong effects on momentum and mass transfer during low wind episodes.

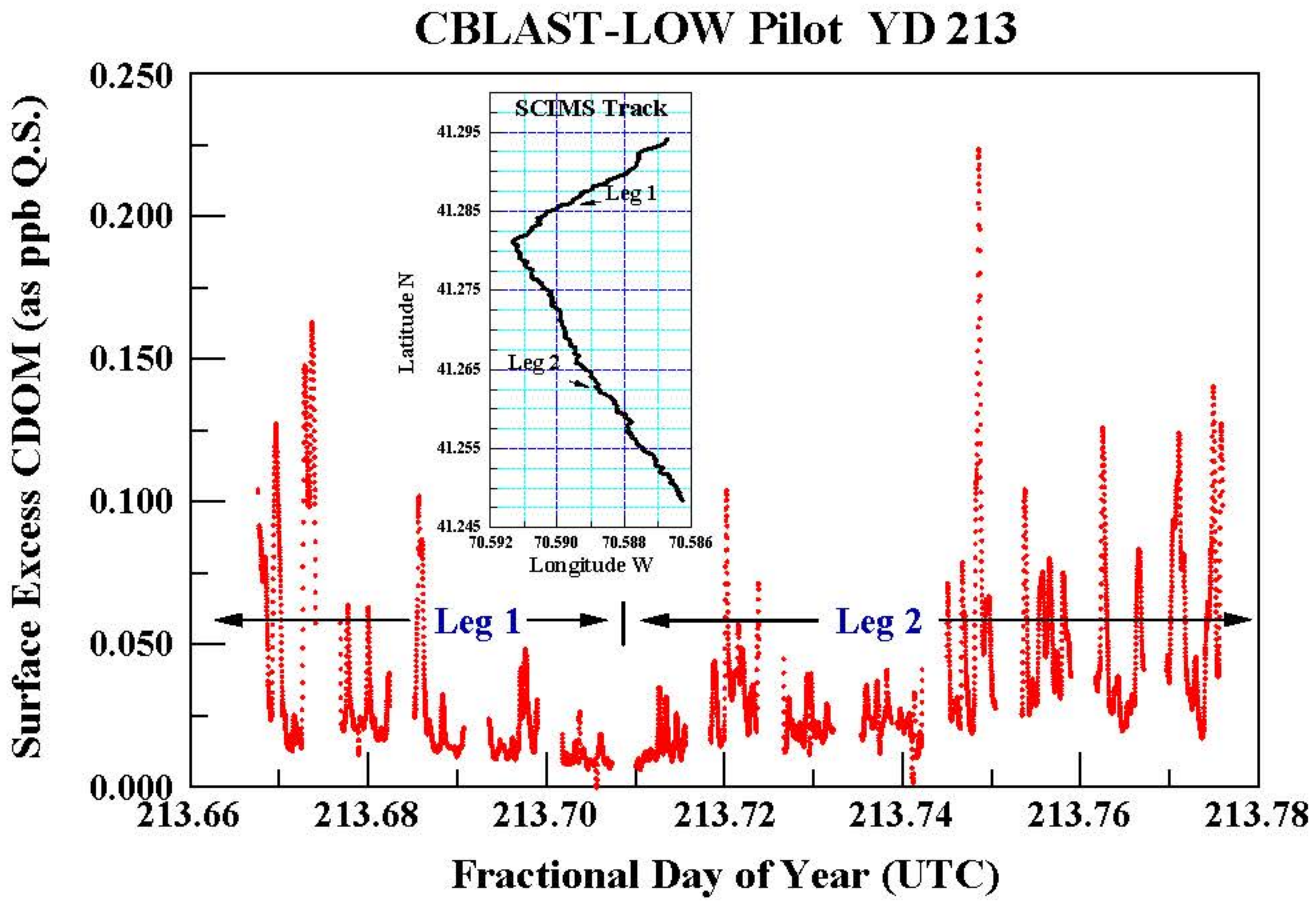

Figure 1: The variation of surface excess colored dissolved organic matter (CDOM) along SCIMS track (inset) during the August 1, 2001 (yearday 213) CBLAST-LOW deployment ranges from 0.01 to 0.23 part per billion (as quinine sulfate). Inset shows two legs of SCIMS track located south of Martha's Vineyard.

During the R/V Oceanus deployments in the MVCO area, a shipboard ion trap mass spectrometer was used to provide a preliminary look at film composition. As an example, the averaged mass spectrum of one extract in a series collected on yearday 179 at 41°14.18' N, 70°38.16' W is shown in Figure 2. This single stage mass spectrum (obtained with electrospray ionization) is clearly complex, with a broad envelope of ions in the scan range of 100-1000 amu, representing primarily singly-charged (protonated or sodiated) parent ions, with a maximum abundance in the molecular weight range of 800-1100 amu. Prominent ions from a series of several unknown but related compounds are observed at 777, 819, 939, 981, 1023 and 1078 amu. Low mass defects along with mass differences of Δ162 amu and Δ42 amu suggest the presence of glycosyl (sugar) moieties in these structures. A more complete identification is being pursued using a combination of ionization modes (electron impact, chemical ionization and electrospray) and multistage (MS^n) mass spectral techniques.

IMPACT/APPLICATIONS

Deployment of the combined sampling package and ion trap mass spectrometer provides the capability to examine the molecular identity and concentrations of organic compounds in the sea surface microlayer and to make better estimates of surface elasticity. The availability of such information during field studies will allow more detailed investigations of air-sea interactions and improved groundtruthing of microwave remote imagery. More rapid information acquisition will allow process studies of links between biology, surfactant production and film distributions, the role of hydrodynamic processes in film formation and dispersal, photochemical degradation processes in the microlayer, and the relative importance of insoluble lipid and soluble biopolymeric surfactants in determining sea surface viscoelasticity. Expected major applications include studies of the role of the marine microlayer in modulating small-scale waves and microwave scattering, microwave signatures of internal waves, wind stress-drag relationships, and turbulent surface renewal and air-sea gas exchange.

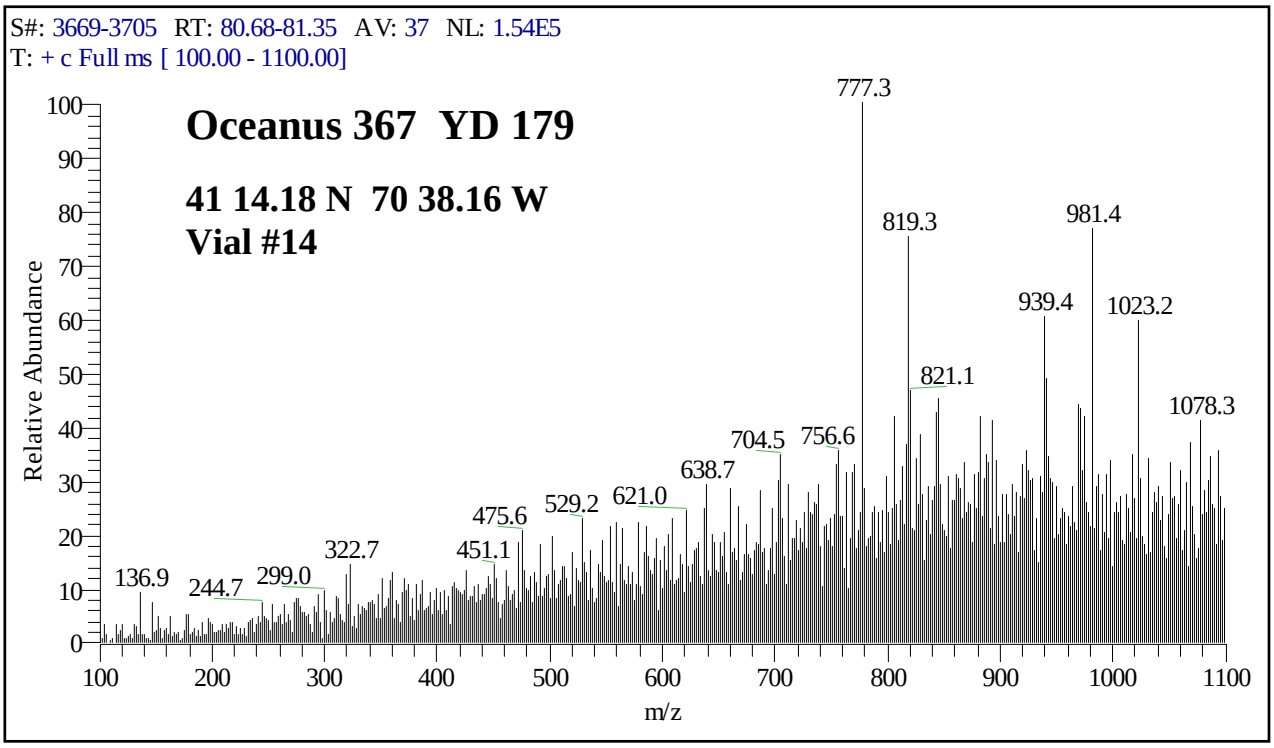

Figure 2: The electrospray ionization mass spectrum of a SCIMS surface microlayer extract shows a broad envelope of ions from 100-1100 amu, with several prominent ions that suggest the presence of glycosylated compounds.

TRANSITIONS

None as yet.

RELATED PROJECTS

This project is closely related to my NOAA-funded effort to understand the role of wind stress, small scale waves, near-surface turbulence, and surface films in modulating air-sea gas exchange (with T. Hara, U. Schimpf, and B. Jaehne) and to my NASA-funded effort to develop algorithms to quantify air-sea gas exchange using remotely-sensed surface roughness (with D. Glover). A collaboration with investigators (J. Edson and others) involved in the CBLAST-LOW initiative to model boundary layer fluxes is also ongoing.

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Frew, N. M., R. K. Nelson, and C. G. Johnson (2002). Sea-slicks: variability in chemical composition and surface elasticity. To be published in *Surface Slicks and Remote Sensing of Air-Sea Interactions*, M. Gade, J. Scott and N. Thomas (eds), Springer-Verlag.

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